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(71) Applicant: **DIRECTOR-GENERAL OF THE AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY**
3-1, Kasumigaseki 1-chome
Chiyoda-ku
Tokyo (JP)

(72) Inventor: **Oishi, Shoji**
817-7, Azuma 2-chome
Tsukuba-shi,
Ibaraki-ken (JP)

(74) Representative: **Allam, Peter Clerk et al**
LLOYD WISE, TREGEAR & CO.
Norman House
105-109 Strand
London WC2R 0AE (GB)

(54) Secondary ion mass spectrometric analysis of metals and method of preparing standard sample therefor.

(57) A method of analyzing a metal-containing sample by secondary ion mass spectrometry for the determination of the concentration of the metal is disclosed. The material is first formed into a solution and a drop thereof is placed onto an electrically conductive surface of a supporting disc. After drying, the resulting solid layer on the supporting disc is subjected to a secondary ion mass spectrometric analysis. When the sample is a liquid, the liquid may be directly placed on the supporting disc. This technique is applicable for the preparation of a standard sample having a known composition of metals and used for constructing a calibration curve.

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This invention relates to a method of analyzing a metal component-containing sample for the determination of the concentration of the metal by secondary ion mass spectrometry and to a method of preparing a standard sample for use in such a secondary ion mass spectrometric analysis.

Ion mass spectrometric analysis has been applied to a variety of solid materials such as films, metals and dusts. In this technique, a sample is bombarded with an ion beam of, for example, 5-15 KeV Ar^+, to cause neutral atoms and ions to be ejected from the sample. The positive ions are extracted into a mass spectrometer and analyzed. Details of this technique are disclosed in, for example, Morrison, G. H. et al, Analytical Chemistry, 47, 933 (1975) and Ishizuka, T., Analytical Chemistry, 46, 1487 (1974).

The conventional method using the secondary ion mass spectrometry has a problem because it cannot be applicable for the analysis of an insulating sample. While incorporation of carbon into the sample could solve the problem of static charging, another problem would arise because the carbon adversely affects the resolution of the mass spectrum. The conventional method poses a further problem because the intensity of the secondary ion varies when the sample is not homogeneous. This will be easily appreciated since the sample is bombarded with a micro beam. Additionally, in the conventional method, a relatively large amount of a sample is required. Thus, unless the sample to be analyzed available in a large amount, it is not possible to adopt the secondary ion mass spectrometric analysis.

In order to obtain exact quantitative analytical data by secondary ion mass spectrometric analysis, it is necessary to prepare a calibration curve using a standard sample having a known composition. No satisfactory method is, however, known in the art which can prepare a desired standard sample matching a sample to be measured.

The present invention has been made in view of the above problems.

There is provided in accordance with one aspect of the present invention a method of analyzing a solid, metal component-containing material by secondary ion mass spectrometry for the determination of the concentration of said metal, comprising the steps of:

(a) mixing said material with a liquid to dissolve said metal component in said liquid and to obtain a solution containing said metal;

(b) placing a drop of said solution onto an electrically conductive surface of a supporting disc;

(c) drying said drop to form a solid layer on said supporting disc; and

(e) subjecting said solid layer on said supporting disc to a secondary ion mass spectrometric analysis.

In another aspect, the present invention provides a method of analyzing a metal component-containing solution by secondary ion mass spectrometry for the determination of the concentration of said metal, comprising the steps of:

(a) placing a drop of said solution onto an electrically conductive surface of a supporting disc;

(b) drying said drop to form a solid layer on said supporting disc; and

(c) subjecting said solid layer on said supporting disc to a secondary ion mass spectrometric analysis.

The present invention also provides a method of analyzing a gaseous, metal component-containing material by secondary ion mass spectrometry for the determination of the concentration of said metal, comprising the steps of:

(a) contacting said material with a liquid to dissolve said metal component in said liquid and to obtain a solution containing said metal;

(b) placing a drop of said solution onto an electrically conductive surface of a supporting disc;

(c) drying said drop to form a solid layer on said supporting disc; and

(e) subjecting said solid layer on said supporting disc to a secondary ion mass spectrometric analysis.

The present invention further provides a method of preparing a standard sample for use in secondary ion mass spectrometric analysis, comprising the steps of:

(a) providing a solution of a first, reference metal or a compound thereof and at least one second metal or a compound thereof having a predetermined composition;

(b) placing a drop of said solution onto an electrically conductive surface of a supporting disc; and

(c) drying said drop to form a solid layer on said supporting disc.

The present invention will now be described in detail below with reference to the accompanying drawings, in which:

Fig. 1 is a calibration curve prepared using a standard sample obtained in Example 1 and showing a relationship between the ion intensity ratio ($^{48}Ti^+/^{56}Fe^+$) and the concentration of Ti based on Fe; and

Fig. 2 is a calibration curve prepared using a standard sample obtained in Example 1 and showing a relationship between the ion intensity ratio ($^{51}V^+/^{56}Fe^+$) and the concentration of V based on Fe.

The present invention is directed to a method of the quantitative analysis of a metal-containing material by using a secondary ion mass spectrometer. Any commercially available ion micro analyzer (or ion microprobe mass analyzer) may be suitably used for the purpose of the present invention. Examples of

such analyzers include Hitachi Ion Micro Analyzer (Hitachi Co., Ltd., Japan), The GCA Ion Microprobe Analytical Mass Spectrometer (GCA Technology Division, USA) and CAMECA IMS ion microscope (CAMECA Inc., France).

When the sample to be measured is a solid, metal component-containing material, the sample is first mixed with a suitable liquid to dissolve the metal component and to obtain a solution containing the dissolved metal. The metal component in the sample may be in the form of an elemental metal or a metal compound. The liquid to be used for the dissolution of the metal may be, for example, an aqueous acid solution such as aqueous nitric acid, sulfuric acid or hydrochloric acid. Any metal and metal compound may be analyzed in accordance with the method of this invention. Examples of such metals include Fe, Mn, Ti, V, Cr, Cu, Ni, Mg, Sn, Ga, Ta, Al, Zr, Cd, Pb, In, Zn, As, Ca, Mo, rare earth elements and mixtures two or more thereof.

The solution is then placed on an electrically conductive surface of a supporting disc. The amount of the solution placed on the disc is optional and is generally 0.00001 ml to 1 ml, preferably 0.0002 ml to 0.05 ml. Suitably, a drop of the solution is placed on the disc with the use of a sylinge or a capillary tube. The disc may be formed of carbon (graphite), silicon or a metal such as Cu, Au or Ag. Alternatively, the disc may be a composite plate composed of an electrically insulating substrate and an electrically conductive layer provided over the surface of the substrate. The size of the disc varies with the size of a holder of the ion microanalyzer used. Generally, the disc has a diameter of 5-30 mm and a thickness of 0.5-3 mm.

It is preferred that that portion of the disc on which the solution is to be applied be previously treated with ethanol for reasons of improved compatibility of the disc surface with the solution. Thus, the surface of the disc is wiped or applied with ethanol and then dried so that the treated portion has improved hydrophilicity. By this expedient, the drop of the solution can be uniformly applied on the disc.

The solution placed on the disc is then dried to form a solid, metal-containing layer. The drying is generally performed at a temperature from room temperature to 150°C, preferably 60-80°C.

When the sample to be measured is a liquid, metal component-containing material, the sample is applied as such onto an electrically conductive surface of a disc and then dried in the same manner as above.

When the sample to be measured is a gaseous, metal component-containing material, the sample is contacted with a liquid such as an aqueous acid solution to dissolve the metal component in the liquid. The resulting solution is then applied on an electrically conductive surface of a disc and dried in the same manner as above. A high temperature waste gas containing Cd, Pb, Zn, Sn, As, Ca or a compound thereof (e.g. $SbCl_3$, $MoCl_3$ or $FeCl_3$) which is vaporized at a temperature in the range of, for example, 150°-300°C may be a typical example of the gaseous sample.

The disc bearing the solid layer is then mounted on a holder of an ion microanalyzer and is bombarded with a micro beam to measure the ion intensity in any suitable known manner.

The above technique can be applied for the preparation of standard samples used for preparing calibration curves. Thus, a solution of a first, reference metal (M_1) or a compound thereof and a second metal (M_2) or a compound thereof having a predetermined composition is first prepared. The solution is then applied onto an electrically conductive surface of a supporting disc and thereafter dried in the same manner as the above, thereby obtaining the desired standard sample having known composition of the metals M_1 and M_2. In this case, it is advantageous to prepare a standard sample containing one standard metal and a plurality of metals having known composition so that the standard sample may be commonly used for the analysis of various metals.

By preparing various standard samples with different metal concentrations and by analyzing these samples with the secondary ion mass spectrometer, a calibration curve representing a relationship between an ion intensity ratio (M_2^+/M_1^+) and a relative concentration of M_2 in M_1 can be obtained. Using the thus prepared calibration curve, the concentration of metal M_2 in a sample containing metals M_1 and M_2 can be determined according to the method of the present invention. In this case, the concentration of the reference metal M_1 should be determined by another method such as ICP-AES (inductively coupled plasma-atomic emission spectrometry).

When the sample to be measured contains Fe, it is recommendable to use Fe as the reference metal for the standard samples. However, any metal may be used as the reference metal of standard samples, irrespective of whether or not the metal is contained in the sample to be measured. For example, Y (yttrium) may be used as the reference metal of standard samples for the analysis of yttrium-free samples. In this case, the reference metal should be incorporated as an internal standard into the samples to be measured.

The following examples will further illustrate the present invention.

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Example 1

Dust sample obtained from a dust separator of an iron sintering furnace was analyzed for the amounts of Mn, Ti, V and Cr according to the method of the present invention. The dust sample was first analyzed by ICP-AES to reveal that the iron content was 42 % by weight.

Preparation of Standard Samples:

Metallic iron was dissolved in hydrochloric acid to obtain an aqueous stock solution having an iron content of 1 % by weight (as elementary iron). A quantity of a second metal M_2 (Mn, Ti, V or Cr) was dissolved in 10 ml of the stock solution. A drop (0.002 ml) of the resulting second metal-containing solution was applied on a graphite disc having a diameter of 10 mm and a thickness of 1 mm and the disc was placed in an oven to dry the solution at 60°C. The above procedure was repeated in the same manner as described with various amounts of respective second metals.

Construction of Calibration Curves:

The thus prepared standard samples were subjected to secondary ion mass spectrometry using Ion Microanalyzer IMA-2 (manufactured by Hitachi Ltd.) to measure the ion intensities M_2^+ and Fe^+. The ratios M_2^+/Fe^+ were plotted against the concentrations of M_2 (% by weight) based on Fe to form calibration curves. Figs. 1 and 2 illustrates the calibration curves of Ti and V, respectively.

At a signal to noise ratio (S/N ratio) of 2, the detection limits of Ti and V were found to be 0.4 ppm (8×10^{-12} g in 2 μl) and 0.9 ppm (18×10^{-12} g in 2 μl), respectively, in terms of the content based on the weight of Fe.

The operating conditions of the ion microanalyzer were as follows:

Primary ion:	O_2^+
Primary ion accelerating potential:	10 kV
Primary ion current:	0.07-0.3 μA
Primary ion beam spot diameter	800 μm
Degree of vacuum:	1.6-2.1 x 10^{-4} Pa
Slit:	0.5 mm
Multiplier voltage:	1.4 kV

Reproducibility Tests:

A number of similar standard samples were prepared and measured for ion intensities. The standard variation of the ion intensities was as summarized in Table 1 below.

Table 1

Concentration of Second Metal Relative To Iron (μg/g)	Standard Variation (%)	
	Ti	V
1,000	2.1	1.8
3,000	0.85	0.86
10,000	1.2	0.61

Analysis of Dust Sample:

The dust sample was dissolved in a hydrochloric acid/hydrogen peroxide mixed solution. The solution was placed on a graphite disc and then dried in the same manner as that in the preparation of the standard samples. The disc bearing the dried sample was analyzed on the ion microanalyzer to measure ion intensities M_2^+. Based on the M_2^+/Fe^+ ratio, the concentration of M_2 was determined from the calibration

curves. The results are shown in Table 2 together with those determined by ICP-AES.

Table 2

Metal	Secondary Ion Mass Spectrometry of the Present Invention (based on Fe)	ICP-AES (based on Fe)
Fe	-	42 %
Mn	0.64 %	0.59 %
Ti	0.52 %	0.54 %
V	510 ppm	420 ppm
Cr	60 ppm	50 ppm

Claims

1. A method of analyzing a solid, metal component-containing material by secondary ion mass spectrometry for the determination of the concentration of said metal, comprising the steps of:
   (a) mixing said material with a liquid to dissolve said metal component in said liquid and to obtain a solution containing said metal;
   (b) placing a drop of said solution onto an electrically conductive surface of a supporting disc;
   (c) drying said drop to form a solid layer on said supporting disc; and
   (e) subjecting said solid layer on said supporting disc to a secondary ion mass spectrometric analysis.

2. A method as claimed in claim 1, wherein said electrically conductive surface is formed of carbon.

3. A method as claimed in claim 1, wherein said liquid is an aqueous liquid.

4. A method as claimed in claim 3, wherein, before step (b), that portion of said electrically conductive surface on which said drop is to be placed is applied with ethanol and then dried to improve the wettability of said portion with said solution.

5. A method of analyzing a metal component-containing solution by secondary ion mass spectrometry for the determination of the concentration of said metal, comprising the steps of:
   (a) placing a drop of said solution onto an electrically conductive surface of a supporting disc;
   (b) drying said drop to form a solid layer on said supporting disc; and
   (c) subjecting said solid layer on said supporting disc to a secondary ion mass spectrometric analysis.

6. A method of analyzing a gaseous, metal component-containing material by secondary ion mass spectrometry for the determination of the concentration of said metal, comprising the steps of:
   (a) contacting said material with a liquid to dissolve said metal component in said liquid and to obtain a solution containing said metal;
   (b) placing a drop of said solution onto an electrically conductive surface of a supporting disc;
   (c) drying said drop to form a solid layer on said supporting disc; and
   (e) subjecting said solid layer on said supporting disc to a secondary ion mass spectrometric analysis.

7. A method of preparing a standard sample for use in secondary ion mass spectrometric analysis, comprising the steps of:
   (a) providing a solution of a first, reference metal or a compound thereof and at least one second metal or a compound tehreof having a predetermined composition;
   (b) placing a drop of said solution onto an electrically conductive surface of a supporting disc; and
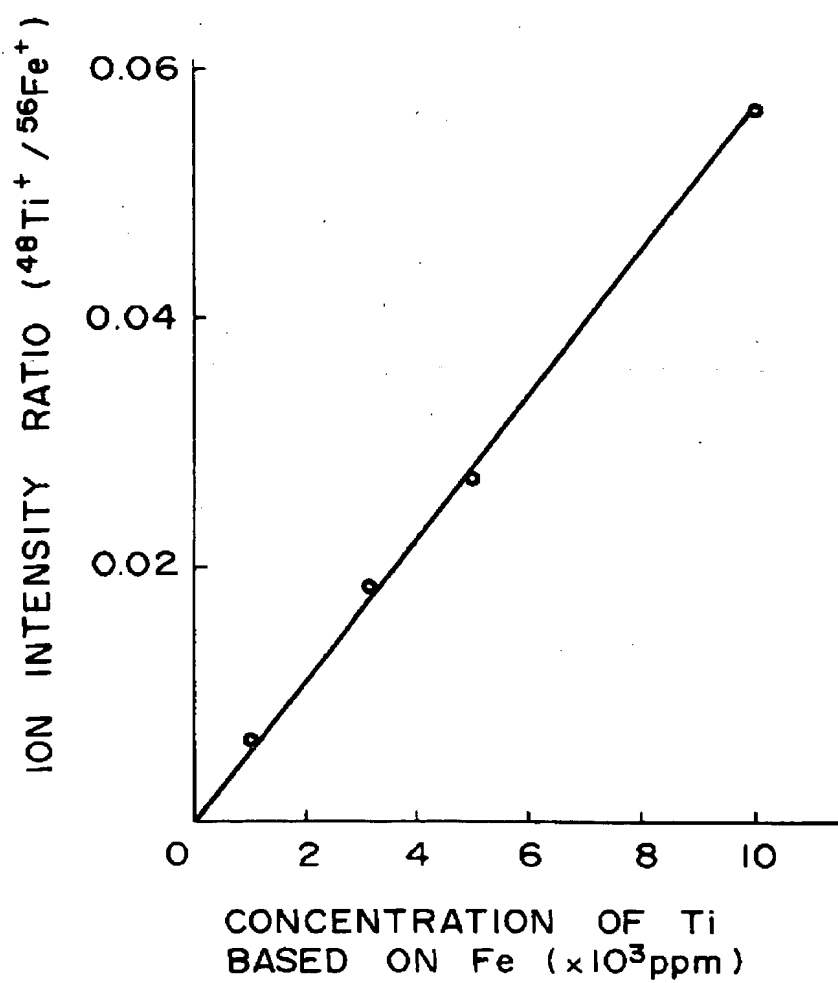   (c) drying said drop to form a solid layer on said supporting disc.

F I G . 1

CONCENTRATION OF Ti
BASED ON Fe ($\times 10^3$ppm)

(Y-axis: ION INTENSITY RATIO ($^{48}Ti^+ / ^{56}Fe^+$); values 0.02, 0.04, 0.06. X-axis: 0, 2, 4, 6, 8, 10)

F I G . 2